STUDY IN COMETARY ASTROPHYSICS

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ABSTRACT

During this period studies on the emission spectra produced by electron bombardment of low pressure gases has continued. The gases studied and the emissions observed include:

$$CH_4 + \varepsilon \longrightarrow C_3,\ CH,\ CH^+,\ H$$

$$C_2H_2 + \varepsilon \longrightarrow C_2,\ CH,\ CH^+,\ H$$

$$CH_3\ C \equiv CH + \varepsilon \longrightarrow C_2,\ CH,\ CH^+,\ H$$

$$CH_2 = C = CH_2 + \varepsilon \longrightarrow C_2,\ CH,\ CH^+,\ H$$

The selective production of C_3 or C_2 from these simple molecules may have important cometary implications. The production of C_3 from CH_4 in these experiments must occur by a very rapid reaction. The intensity of the C_3 emission was found to increase in experiments using low energy electrons. Results of these experiments are presented and discussed.

Studies of the rate of the collisional interchange of the singlet and triplet states of C_2 have continued. Measurements in shock heated cyanogen show that the singlet state is produced more rapidly than the triplet state. A quantitative determination has been made of the steady state concentration levels of singlet C_2 observed. Measurements leading to a rate for the collisional interchange are in progress.

Photochemical decomposition in the far ultraviolet of methyl acetylene at low pressure has been initiated. Photochemical decomposition leads to the formation of molecular hydrogen, atomic hydrogen and acetylene. Molecular hydrogen formation assumes increasing importance relative to other processes at shorter wavelength. Direct production of C_2 from methylacetylene appears to be considerably

less important than it is in the decomposition of acetylene or diacetylene.

INVESTIGATORS

The investigations described in this report have been carried out through the efforts of the following personnel:

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1. SHOCK TUBE STUDIES: Collisional Energy Transfer for Singlet and Triplet States of C_2

The rate of the collisional intersystem crossing for C_2 is important in evaluating the role of molecular collisions in the inner coma of a comet. Work has continued this quarter to determine this rate. Both the b $^1\pi_u$ and X' $^3\pi_u$ electronic states of C_2 were observed last quarter in shock heated cyanogen. Photoelectric recording of the absorption by these electronic states this quarter has resulted in the determination of the steady state concentrations of the b $^1\pi_u$ state. Preliminary evidence for the collisional production of the triplet state from the singlet state is presented and discussed.

1.1 Experimental

The absorption measurements this quarter have been conducted in the 2.5 inch ID aluminum shock tube described in previous reports. A characteristic flash lamp containing 10 torr dimethylmercury was used as the spectral source. This lamp emits the singlet Deslandres-d'Ajambuja system and the triplet Swan system in addition to the strong mercury lines at 3650 Å, 4358 Å, and 5460 Å. Addition of air to the lamp results in very intense CN violet emission. Free of air the lamp contains no measurable CN emission. The lamp output passes through quartz windows located in the wall of the shock tube and is brought to focus on the entrance slits of a Bass-Kessler grating spectrograph. Two movable exit slits are located in the focal plane of the spectrograph camera. 1P28 phototubes are fitted to the exit slits

and their outputs are recorded on the chopped sweep of an oscilloscope. The response time of the phototubes and associated electronics is 5 μsec.

The shock velocities were determined from two platinum heat transfer gauges located 50 mm either side of the absorption windows. The output of the gauges was recorded on a direct reading digital timer which resulted in an velocity measurement accuracy of $\pm$ .2%. Marks from the shock front passing the gauges were also superimposed on the oscilloscope absorption traces so that the time for absorption after passage the shock front could be determined. The signal from a third heat transfer gauge located upstream was used to initiate the flash lamp and trigger the oscilloscope after a preset delay time.

The absorption of the c $^1\Pi_g \longrightarrow$ b $^1\Pi_u$ system of C_2 has been recorded as a function of time this quarter for mixtures of 2.5, 5 and 10 percent cyanogen in argon in the temperature range 2000° K to 2800° K. Absorption of the 3650 Å mercury line was recorded simultaneously to monitor the background absorption. Emission intensities were recorded under similar shock conditions and where necessary were subtracted from the absorption intensities to obtain the correct level of absorption. The spectrometer band pass was 2.0 Å and was set at the head of the (0,0) band at 3852.2 Å which covered the lines J=2 to J=19 in the P branch.

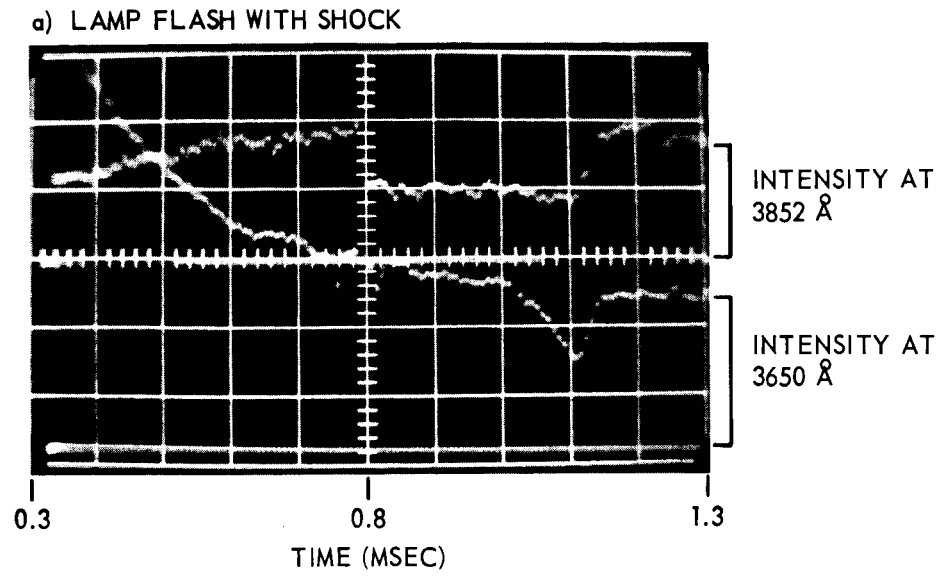
Temporal absorptions of the C_2 Swan band at 5165 Å and the CN violet bands at 3883 Å and 3862 Å are presently under investigation. To date studies have been made in 2.5 and 10 percent mixtures of cyanogen in argon. The C_2 absorption has been recorded simultaneously with the continuum absorption at 4358 Å and 5460 Å, and the CN absorption has been recorded simultaneously with the continuum absorption at 3650 Å.

1.2 Results

C_2 b $^1\Pi_u$ State:

A typical oscilloscope absorption record is shown in figure 1a. The shock front arrives at the absorption windows at a point midway between the gauge marks shown on the lower trace. This trace shows rapid absorption of singlet C_2 at the shock front and a delayed background absorption at 3650 Å. Two flashes of the lamp without absorption are shown in figure 1b.

For all the C_2 singlet records the absorption is observed to rise shortly ($<10\,\mu$sec) after passage of the shock front and level off to a plateau which is maintained until the background absorption begins. The majority of the records show an absorption maxima approximately $50\,\mu$sec after the front with a subsequent decrease to the plateau value. The plateau values of the optical density as a function of measured shock speed are plotted in figure 2. These values have been normalized to a 10 torr (STP) cyanogen shock density before reaction



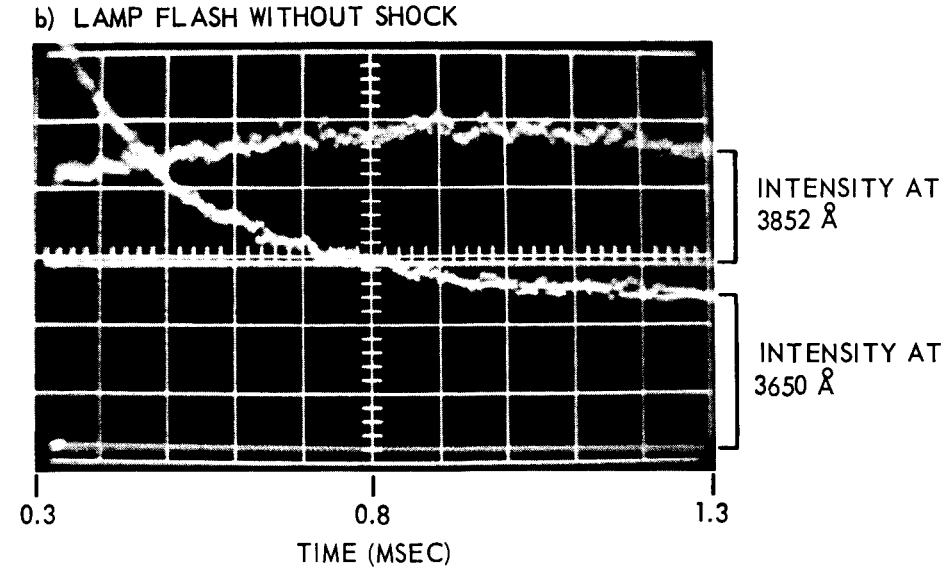


Figure 1. Typical Absorption Record

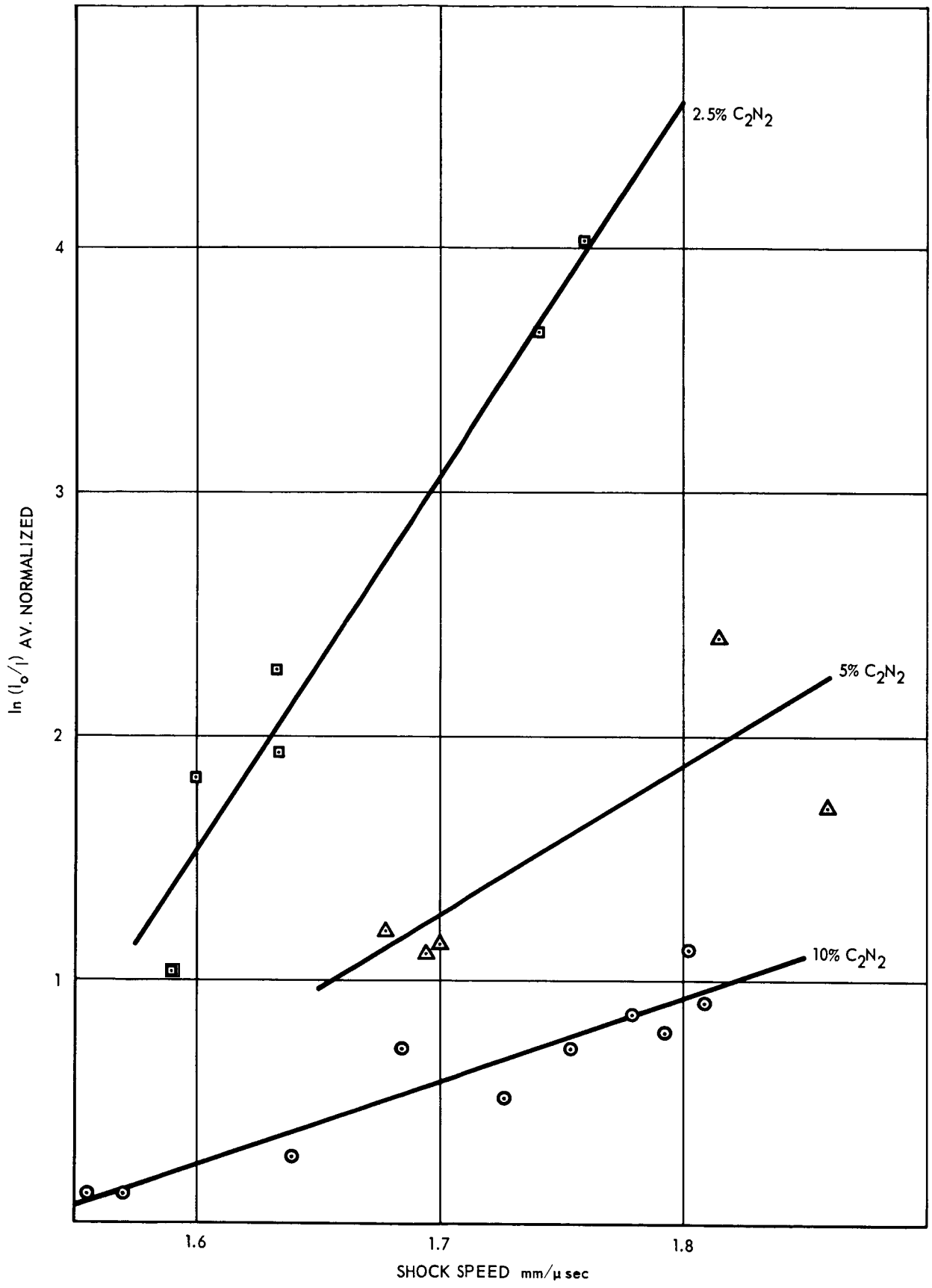


Figure 1. Optical Density vs. Shock Speed

in order to separate the data for different concentration runs. Only the runs for which good velocity measurements were obtained and which showed a good plateau are included in this figure. The shock speeds correspond to the temperature range of approximately 2100° K to 2800° K. These temperature values have been calculated from a real shock tube program assuming no reaction. Accurate shock parameters for these runs must include the effects of chemical reaction. This is discussed in the next section.

The concentrations of the b $^1\pi_u$ state in the shock heated gas can be determined from the optical density measurements as follows. According to Penner[1], we can write

$$\frac{1}{p\ell}\int_{\Delta\omega} \ln(Io/I)\, d\omega = P_{\Delta\omega}\, d\omega \qquad (1)$$

where:

p is the partial pressure in atmospheres of the absorbing molecules

ℓ is the path length in cm

ω is in wavenumbers

$\Delta\omega$ is the spectrometer band pass in wavenumbers

P is the average effective spectral absorption coefficient

We may also write:

$$\int_{\Delta\omega} P_\omega\, d\omega = \frac{\pi e^2 A}{m c^2 R T} f_{l\to u} \qquad (2)$$

where:

A is Avogadro's number

$f_{l \to u}$ is the oscillator strength for the lines in the band pass.

Since a large number of lines cover the entire spectral band, the integral of the absorption coefficient in equation (2) can be replaced by an effective coefficient as in equation (1). The following results:

$$P = \frac{T \ln (Io/I) \Delta\omega \; R \, m \, c^2}{f_{l \to u} \qquad A \, \pi \, e^2} \qquad (3)$$

To obtain the pressure of all the molecules in an electronic state expression equation (3) must be divided by the ratio of the molecules in the absorbing rotational levels to the total population. At equilibrium this can be written:

$$Q_T = \frac{\sum_{J=2}^{19} (2J+1) \, e^{-\varepsilon/RT}}{Qv \;\; Qr} \qquad (4)$$

where:

ε is the energy of the rotational levels

Qr and Qv are respectively the rotational and vibrational partition functions for the absorbing state.

The final expression pertinent to our work on C_2 singlet where $l = 6.48$ cm and $\Delta\omega = 13.6$ cm^{-1} is

$$p(atm) = \frac{(3.46 \times 10^{-10}) \; T \; \ln(Io/I)_{AV}}{Q_T \;\; f_{l \to u}} \qquad (5)$$

The Q_T values pertinent to these studies have been evaluated and range from 0.243 at 2000° K to 0.154 at 2800° K. The average optical density is obtained directly from the photographic

records of the oscilloscope and the temperature is calculated from the measured shock speed. The largest error lay in the choice of the f value for the transition. The only value available for this transition is the theoretical value of 0.065 reported by Clementi[2]. If we assume this value is correct for the entire transition, we must estimate a value pertinent to our measurements since they involve only a relatively small number of lines. Estimating a correction to this value because of absorption in the R branch and in the (1,0) transition we arrive at a value of ≈ 0.03. Using this value the concentrations covered in figure (1) ranges from approximately 8×10^{-3} torr at 2100° K to 0.16 torr at 2800° K. It should be noted that the choice of an oscillator strength will affect the value of the absolute concentrations but will have no effect on the relative concentrations.

C_2, $X' \, {}^3\Pi_u$ and CN, $X \, {}^2\Sigma^+$ States:

Temporal absorption measurements of triplet C_2 reveal a delay time of approximately 200 μ sec for the onset of absorption in a 10% cyanogen - argon mixture at approximately 2800° K. Studies at 4358 Å and 5460 Å shown some background continuum absorption under similar conditions. However, the majority of the absorption is attributed to the C_2 Swan band. One experiment at $T_2 > 3000^{\circ}$ K in a 2.5 percent cyanogen mixture showed a rapid increase in Swan band absorption at the shock front. There is total absorption of the (0,0) CN violet

band at 3883 Å under these conditions. An experiment at 2300° K in a 10 percent cyanogen - argon mixture resulted in a steady state optical density of 1.4 at the CN violet band head at 3862 Å. All the runs show a rapid rise in CN absorption shortly after passage of the shock front.

1.3 Discussion

The shock parameters (temperature, density and pressure) as discussed in the previous section have been calculated from a real gas program assuming no chemical reaction. These values are reliable for the lower temperatures but will deviate from the true values at the higher temperatures because of the high endothermicity of the cyanogen decomposition reaction (ΔH = 125 kcal) and the increased extent of decomposition[3]. The ΔT in the shocked gas due to chemical reaction has been estimated to be as large as -200° K at 2500° K. An equilibrium computer program for calculation of the true shock parameters including effects due to chemical reactions is being sent to us by Cornell Aeronautical Laboratories, Inc. in Buffalo and will be run shortly.

The decomposition of cyanogen in the temperature range studied here has been demonstrated to occur by the second order reaction[3]

$$Ar + C_2N_2 \longrightarrow 2\ CN + Ar$$

We feel that the production of singlet C_2 very close to the shock front suggests that C_2 is being formed by the reaction

$$2\ CN\ (X\ ^2\Sigma^+) \longrightarrow C_2\ (x\ ^1\Sigma_g^+) + N_2\ (X\ ^1\Sigma^+)$$

The $C_2(x\ ^1\Sigma_g^+)$ should equilibrate rapidly with the $C_2(b\ ^1\pi_u)$ state measured here. Another possibility would be direct production of the singlet state from the decomposition of C_2N_2 but this is unappealing since it is difficult to envision a reasonable reaction complex that would decompose to C_2 and N_2. Production from more complex products is ruled out since their concentrations will be low near the shock front. Future rate studies at lower concentrations and higher shock densitites will firmly establish the rate process responsible for the singlet C_2 production.

The steady state concentration levels calculated from the absorption records and reported in the previous section are high but are within reasonable limits for these experiments. The cause of the overshoot of the C_2 singlet absorption ~ 50 μ sec after passage of the shock front is not known. However, one possibility is that it is due to delayed relaxation processes near the front. This assumption is reasonable since for the gas temperature and density range studied here a molecule will suffer only about 10^4 collisions in one microsecond of laboratory test time.

The delay observed for the onset of the C_2 triplet absorption is very encouraging since it does demonstrate a different time dependence for the production of the singlet and triplet states of C_2. The triplet state might be produced directly

from the singlet by a collisional process, directly from reactions of CN radicals, or by decomposition of higher molecular weight products (polymers). One run at a lower concentrations of cyanogen (2.5%) and a higher temperature ($>3000^{o}$ K) has yielded triplet absorption shortly after arrival of the shock front. There was no continuum absorption observed for this run. This experiment suggests that the rate of triplet C_2 production is less strongly dependent on concentration than the rate of polymer production. We therefore presently feel that the C_2 triplet is not produced from polymer intermediates in the shock heated gas. Future rate studies will distinguish between C_2 triplet production by reaction of CN radicals and production from singlet C_2 by a collisional process since the rate will be second order in CN for the former process and first order in singlet C_2 for the latter.

Future studies of the singlet and triplet states of C_2 will place emphasis on the determination of the rates in low concentrations mixtures of cyanogen in argon. This will result in a reduced rate of production of singlet C_2 relative to triplet C_2 and will help eliminate interference due to background continuum absorption. Absorption of the singlet and triplet C_2 states will also be recorded simultaneously in the same shock. The shock parameters will determined from the equilibrium computer program and the absorption records of both the singlet and triplet systems will be analysed as

In addition to information on the rate of the collisional intersystem crossing for C_2, the present work promises to yield information on the rate of production of singlet C_2 from the reaction of CN radicals. This is important to an understanding of cometary processes because of the relatively high concentration of CN in cometary coma. Continued work might also lead to a determination of the oscillator strength for the c $^1\Pi_g \longrightarrow$ b $^1\Pi_u$ system of C_2. This will be possible if the concentrations of singlet C_2 can be determined independently of the optical density data. The equilibrium shock program will be extremely helpful in this respect.

1.4 References

a. S. S. Penner, "Quantitative Molecular Spectroscopy and Gas Emissivites" (Addison - Wesley Publishing Co., London, 1959) p. 20.

b. E. Clementi, Astrophys. J. 132, 898 (60).

c. W. Tsang, S. H. Bauer and M. Cowperthwaite, J. Chem. Phys. 36, 1768(62).

2. EXCITATION OF SPECTRA BY ELECTRON BOMBARDMENT

Excitation of appropriate parent molecules by electron and proton bombardment will produce radicals and ions observed in comets. The importance of corpuscular radiation in the production of the observed species has received some theoretical consideration [1-4] but these have been hampered by the lack of quantitative optical excitation data. Except for some recent work with N_2O[5], the data reported to date relate only to atomic and diatomic systems[6]. A series of experiments, without quantitative cross-section data, has been reported[7] for electron-impact excitation of OH produced from H_2O, H_2O_2 and several alcohols.

Experiments in this laboratory will provide quantitative optical excitation data for important polyatomic molecules which include CH_4, H_2O, NH_3, C_2H_2 and C_3O_2. In addition, oscillator strengths can be measured for any observed system of interest.

During this quarter studies were continued with CH_4 and C_2H_2. In addition, limited studies were carried out with $CH_3C{\equiv}CH$ and $CH_2{=}C{=}CH_2$. Several experiments were carried out with H_2O and mixtures of $H_2O{+}CH_4$ but no analysis of these experiments are available at this time.

2.1 Experimental

The electron bombardment studies were carried out in a high vacuum system containing an electron gun and a collision chamber, isolated from one another by apertured disks. The chambers were differentially pumped by four-inch diffusion pumps with a pumping speed of 150 l/sec, equipped with liquid nitrogen cooled zeolite traps. The system was capable of producing a vacuum

less than 10^{-7} torr. During gas bombardment, the pressure in the gun chamber could be maintained in the 10^{-6} torr region. The residence time for a molecule in the chamber was in the range of 10^{-6} - 10^{-7} sec.

The gas under study was introduced into the collision chamber through a servo-controlled leak sensing on a capacitance type micromanometer. The manometer measured the pressure in a small bore tube leading to the collision chamber. Nominal operating pressures in the collision chamber were from $1x10^{-4}$ to $5x10^{-2}$ torr as recorded by a pair of thermistors in the chamber. The emission produced from the interaction of the gas and electron beam was monitored through a sapphire window opposite a screened aperture cut in the side of the collision chamber.

The collision chamber and electron collector were mated to an electron gun built from a commercial gun kit (Nuclide type 606). The gun employed a tungsten ribbon filament operated at 1800°K. The filament was located 0.7cm from the collision chamber, the intervening space being occupied by accelerating and focusing grids. Electron energies from 70 to 500 ev could be obtained in the collision chamber at up to 500 ua. The vacuum baffle between the gun and collision chamber effectively limited the amount of scattered filament light seen by the spectrometer.

The emission spectra were recorded photometrically using both a Bausch and Lomb (f/3.5) grating monochromator and a Jarrell-Ash 0.5 Meter Ebert Scanning Spectrometer (f/8.6). The B&L monochromater was motor driven with the photomultiplier and wavelength outputs driving an X-Y plotter. The monochromator was used for gross spectra studies in the wavelength region

from about 2000 Å to 6000 Å. The 0.5 meter Ebert was used for high resolution studies in the same wavelength region. This instrument has at least 0.2A resolution in first order with a 1180 grooves/inch grating.

2.2 Results and Discussion

Molecules studied this quarter include CH_4, C_2H_2, $CH_3C{\equiv}CH$ and $CH_2{=}C{=}CH_2$. To date, the most extensive data has been taken with CH_4, but due to the complexity of the experimental system and the results, the data is only very qualitative. The data obtained with the other molecules is likewise only qualitative. The molecules studied do not appear to have similar excitation cross sections and definitely do not produce similar emission spectra.

2.2.1 Methane, CH_4

Photoelectric recordings of these emissions were taken from about 2000-6000 Å over a pressure range 10^{-3} - 10^{-4} torr. Scanning speeds used were 500 Å and 50 Å/min. The electron energies were varied from 80-250 eV. Emissions were observed from atomic hydrogen, CH, CH^+ and C_3. The emission of each species was very dependent on the pressure, electron energy and gun current. The most intense emission observed under most conditions was due to the CH radical. The electronic transitions observed were:

CH	$A^2\Delta \longrightarrow X^2\Pi$
	$B^2\Sigma \rightarrow X^2\Pi$
CH^+	$\Pi \longrightarrow \Sigma$
C_3	$\Pi \longrightarrow \Sigma$
H	Balmer Series

A series of experiments were carried out to investigate the general conditions for C_3 production. It was found that the emission increased with pressure and decreasing electron energy. The pressure and electron energy range covered for these experiments was 20 to 35μ and 80 to 250 eV respectively. Increasing the beam current for a given value of pressure and electron energy also increases the 4050 Å emission. This latter effect is probably due to an increase in the number of reacting particles and not to a mechanism change. The effect observed with electron energy probably indicates different species are responsible for the C_3 emission which are favored by low energy electrons.

2.2.2 Acetylene, CH=CH

Photoelectric recording of the emissions produced from electron bombardment of acetylene were made over the pressure range of 2-20μ . The beam current and electron energy was 180μa and 250 eV respectively. Scanning was made at 500 Å/min. Emissions were observed from atomic hydrogen, CH, CH^+ and C_2. The electronic transitions observed were:

CH	$A^2\Delta \longrightarrow X^2\Pi$
	$B^2\Delta \longrightarrow X^2\Pi$
CH^+	$\Pi \longrightarrow \Sigma$
C_2	$A^3\pi \longrightarrow X^3\Pi$
H	Balmer Series

The C_2 Swan bands are relatively strong in these experiments. The High Pressure system is also found in comparable intensity. On the basis of these experiments it is expected that the C_2 singlet system is also being formed

and will be observed when the infrared region is examined.

2.2.3 Methylacetylene, $CH_3C{\equiv}CH$

Photoelectric recording of these emissions were taken from about 2000-6000 Å over a pressure range of 2 to 20 μ with a scanning speed of 500 Å/min. The beam currents used ranged from 280 to 510μa with 250ev electrons. Emissions were observed from atomic hydrogen, CH, CH^+ and C_2. The electronic transitions observed for these radicals were identical to the acetylene experiments with the exception that C_2 Swan bands are not excited. The C_2 high pressure bands are present.

2.2.4 Allene, $CH_2{=}C{=}CH_2$

Photoelectric recording of these emissions were taken from about 2000-6000 Å over a pressure range of 30 to 35μ with a scanning speed of 500 and 50 Å/min. The beam currents were from 160 to 500μa with 250 eV electrons. Emissions were observed from atomic hydrogen, CH, CH^+ and C_2. The electronic transitions observed for these radicals were identical to the acetylene experiments. However, with allene, the C_2 system appears with greater intensity.

2.3 References

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3. PRIMARY PHOTOCHEMICAL PROCESSES: METHYLACETYLENE

The free radicals observed in comets could be produced by the simple photodissociation of parent molecules. To provide information on the interaction of solar photons with these parent compounds, we have been evaluating in the laboratory the importance of various primary processes in the photolysis of the simple molecules CH_4, H_2O, and NH_3. More reactive molecules have also been under investigation and have included H_2O_2, N_2H_4, C_2H_2, etc., since they are related and can be synthesized readily from the molecules of primary interest.

During this quarter, the photolysis of methylacetylene (C_3H_4) has been examined to evaluate its role as a potential source of the C_3 radical in the coma of comets. Experiments will be performed using both near and far ultraviolet radiation. To date, we have studied the photochemical reaction of methylacetylene in the banded region[1] (1050 to 1600 Å), using the 1236 Å Kr line and the 1470 Å Xe line. Future experiments will examine the photochemical reactions in the continuum (1600 to 2000 Å) using the 1849 Å Hg line.

The only available information regarding photochemical decomposition of methylacetylene is that photolysis in the near ultraviolet[2] of the pure compound at 77°K results in the formation of the 2-propynyl radical (propargyl radical), presumably formed in the process,

$$CH_3C \equiv CH + h\nu \longrightarrow CH_2C \equiv CH + H \qquad (1)$$

3.1 Results

Photolysis of methylacetylene in the region 1 to 10 torr leads to extensive polymer formation and a drastic decrease in the transmission of the window of the photolysis cell. To avoid this complication, we have restricted our attention to the pressure region of 0.2 torr of the pure compound where polymer formation is less extensive. Quantum yields of product formation and for disappearance of methylacetylene have been determined. The effect of N_2 and C_2D_4 has been examined in the photolysis at 1470 and 1236 Å.

3.1.1 Photolysis at 1470 Å Xe Line

The results are shown in Table 1. The major products H_2 and C_2H_2 are formed in nearly equal amounts (ϕ = 0.2). The quantum yield for the disappearance of methylacetylene is approximately 0.50. Methane is a very minor product.

The quantum yield for H_2 formation is reduced by about 40% in the presence of C_2D_4, without effecting CH_4 production or methylacetylene decomposition. Addition of 1 torr N_2 does not prevent decomposition of methylacetylene, although the yield of C_2H_2 is reduced. Ethane, ethylene, and propylene are also formed in low yield. The material balance is poor ($C_3H_{7.2}$) indicating formation of carbon-rich products (polymer?).

3.1.2 Photolysis at 1236 Å Kr Line

The results are shown in Table 2. The major products are still H_2 and C_2H_2, although the H_2 yield is now twice the C_2H_2 yield. The quantum yield for methylacetylene decomposition is close to 0.25.

TABLE 1

1470 Å PHOTOLYSIS OF METHYLACETYLENE

Pressure (millitorr)			Quantum Yield (molecules/quantum)				
$CH_3C \equiv CH$	N_2	C_2D_4	H_2	CH_4	C_2H_2	C_2H_6	$-CH_3C \equiv CH$
190	0	0	0.23	0.02	0.19	0.08	0.5
190	0	0	0.26	0.02	0.22	0.08	0.6
190	1,000	0	n.d.	n.d.	0.09	0.04	0.4
190	1,000	0	n.d.	n.d.	0.10	0.05	0.5
190	0	23	0.15	0.02	n.d.	n.d.	0.4

C_2H_4 and C_3H_6 were also observed in most experiments; quantum yield was less than 0.04.

n.d. = not determined.

TABLE 2

1236 Å PHOTOLYSIS OF METHYLACETYLENE

Pressure (millitorr)			Quantum Yield (molecules/quantum)				
$CH_3 C \equiv CH$	N_2	C_2D_4	H_2	CH_4	C_2H_2	C_2H_6	$-CH_3 C \equiv CH$
190	0	0	0.15	0.01	0.08	0.01	0.24
190	0	0	0.18	0.01	0.10	0.01	0.23
190	1,000	0	n.d.	n.d.	0.03	$<$0.01	0.26
190	0	21.5	0.17	0.01	n.d.	n.d.	0.35

C_2H_4 and C_3H_6 were also observed in most experiments; quantum yield was less than 0.03.

n.d. = not determined.

Methane is still a very minor product. Present results suggest that addition of 20% C_2D_4 has no effect on the H_2 formation. Addition of 1 torr N_2 does not reduce methylacetylene decomposition; but, as before, reduces the acetylene formation. Ethane is a less important product at this wavelength. Ethylene and propylene are detected in low yield. The material balance ($C_3H_{7.8}$) again suggests formation of carbon-rich products.

3.2 Discussion

The very low yield of CH_4 demonstrates that the molecular elimination process

$$CH_3\ C \equiv C\ -H + h\nu \longrightarrow C_2 + CH_4 \qquad (2)$$

which is analogous to that suggested for C_2H_2[3] and C_4H_2[4], is of little importance in these experiments. The present discussion will be limited to potential processes leading to the major products (H_2 and C_2H_2).

3.2.1 Molecular Formation of Hydrogen

The substantial yield of H_2 in the presence of 20% C_2D_4 (which is an effective H atom acavenger) suggests the occurrence of primary process I, with H_2 being removed from either the same carbon or from the terminal carbon atoms:

$$CH_3\ C \equiv CH + h\nu \longrightarrow H_2 + .\overset{H}{\underset{\cdot}{C}} - C \equiv CH \qquad \text{Ia}$$

$$CH_3\ C \equiv CH + h\nu \longrightarrow H_2 + .CH_2\ C \equiv C. \qquad \text{Ib}$$

We will attempt an evaluation of these two processes by studying the photolysis of $CD_3\ C \equiv CH$. Photolysis of this compound (in the presence of C_2H_4) should yield D_2 according to process Ia and HD according to process Ib. Hydrogen formation in the presence of ethylene could also result from reaction of hot H atoms. The hydrogen isotopes formed in photolysis of mixture of $CD_3C \equiv CH$ and $CH_3C \equiv CH$ in the absence and presence of ethylene will be examined to test this possibility.

It is interesting to note that molecular hydrogen formation assumes increased importance at the shorter wavelength and is evidently the sole source of H_2 at 1236 Å.

3.2.2 Formation of Atomic Hydrogen

The reduction in H_2 yield upon addition of ethylene suggests the occurrence of the prime process II with elimination of either the paraffinc or acetylenic hydrogen.

$$CH_3\ C \equiv CH + h\nu \rightarrow \begin{cases} \cdot CH_2\ C \equiv CH + H & \text{IIa} \\ CH_3\ C \equiv C\cdot + H & \text{IIb} \end{cases}$$

Both will be followed by the adstraction reaction

$$H + CH_3\ C \equiv CH \longrightarrow H_2 + \cdot CH_2\ C \equiv CH \qquad (3)$$

Process IIa has been observed[2] for $\lambda > 2000$ Å. We will attempt to evaluate the relative importance of these processes by the use of $CD_3\ C \equiv CH$. Process IIa (followed by 3) will yield D_2, while process IIb (followed by 3) will yield HD. Correction will be made, of course,

for the nonscavengeable isotopic hydrogens based on the results obtained in the presence of ethylene.

3.2.3 Acetylene Formation

The formation of acetylene in the photolysis of methylacetylene may be attributed to direct molecular elimination

$$CH_3\ C \equiv CH + h\nu \longrightarrow CH_2 + C_2H_2 \qquad \text{IIIa}$$

or to formation of ethynyl radicals

$$CH_3\ C \equiv CH + h\nu \longrightarrow CH_3 + C_2H \qquad \text{IIIb}$$

followed by the astraction reaction

$$C_2H + CH_3\ C \equiv CH \longrightarrow C_2H_2 + \cdot CH_2\ C \equiv CH \qquad (4)$$

While C_2H reacts readily with alkanes[5] and alkenes[6] (and presumably alkynes), it apparently is unique among free radicals in its lack of reactivity[5] with NO. Scavenging of C_2H would thus have to be achieved with a large excess of compound which is transparent at 1470 Å. Methane immediately suggests itself for this purpose. Addition of sufficient CD_4 to cause the reaction

$$C_2H + CD_4 \longrightarrow C_2H\ D + CD_3 \qquad (5)$$

should result in the replacement of C_2H_2 product by C_2HD. It will have to be determined whether there is a pressure effect by examining the photolysis in the presence of N_2 at a pressure equal to that used in the CD_4 experiment.

With regard to the possible occurrence of process IIIa, it should be noted that, in the presence of C_2D_4, cyclopropane-d_4 and/or propylene-d_4 should be formed by insertion of methylene into the double bond of ethylene. This has not been observed, although with 20% C_2D_4 the principal fate of CH_2 may still be reaction with methylacetylene.

3.3 References

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